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Koichi Matsubara.

PROFESSOR KOICHI MATSUBARA.

Professor Koichi Matsubara was born in Nagoya as the first son of Yasoichi Matsubara, a *samurai* of the Owari clan, on the 22nd day of the fifth month of the fifth year of Meiji in the then statutory lunar calendar, corresponding to June 27, 1872, in the Gregorian calendar. He came to Tokyo in his sixth year of age and received all his educations in Tokyo. Thus, in 1878, he was first sent to Nankai-Gakko and then to Shiba-Gakko, both municipal elementary schools in the city, and in 1884, he went to Tokyo Prefectural Middle School. In 1888, he was admitted to the First Higher Middle School, in whose dormitory he lived for five years. In 1893, he graduated from this school and was matriculated at the College of Science of the Imperial University of Tokyo, where he chose chemistry as his speciality and studied under Professors Divers, Sakurai, Haga, Yamagawa, Fujisawa, and Tsuruta. In 1896, he finished his university course, and continued his studies as a post-graduate student.

In 1897, he was appointed to the professorship at the Second Higher School in Sendai, and took the charge of chemistry in the preparatory courses for imperial universities, the main courses in the Higher Schools at that time. In the next year, he was transferred to the same post in the First Higher School in Tokyo. In 1899, he was appointed Assistant Professor of Chemistry in the College of Science of the Imperial University of Tokyo. Being sent to Europe, as a Government Research Fellow, for further study of organic chemistry, he spent two years, from 1903 to 1905, at Owens College of the University of Manchester, under Professor W. H. Perkin, working on nor-terpene, etc., and next one year at the University of Berlin, under Professor Emil Fischer, working on valine, etc. He came back to his *alma mater* in 1906, and the chair of organic chemistry in the College of Science was put in his care. This chair he held for twenty-seven years continuously since then. In 1909, he was promoted to the Professorship, and in 1913, the degree of D. Sc.

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was conferred to him by the Minister of Education upon the recommendation of the President of the Imperial University of Tokyo. From 1913 to 1929, he gave the lectures on organic chemistry also to the students of the Department of Applied Chemistry in the College of Engineering of the University. He was elected by his Faculty a Member of the Library Committee of the University from 1913 to 1930, and was elected its Chairman in 1927 and 1929. In December of 1926, he was elected a Member of the University Council for three years, and in December of 1929, he was appointed the Dean of the Faculty of Science. May 22, 1932, being his sixtieth birthday, he retired from the Professorship and the Deanship on March 31, 1933, the end of the academic year, in accordance with the traditions concerning the age limit of professors in the Imperial University of Tokyo. Quite recently, the title of Honorary Professor of the Imperial University of Tokyo was conferred to him by Imperial command. He is in the Senior Third Court Rank, and is decorated with the Second Class of the Imperial Order of the Sacred Treasure. He was one of those whose meritorious services for the sake of education extending over thirty years were specially honoured by the Minister of State for Education on the 10th of November, 1928, the Coronation Day of the present Emperor.

Professor Matsubara was requested by the Ministry of Education to serve on several committees, some nominated by the Imperial Cabinet upon the recommendation of the Minister of Education and others nominated by the Minister.

Thus he was nominated by the Cabinet an Additional Member of the Committee for the Compilation of the Catalogue of Scientific Literature in 1901, and served as such for two years. He was again nominated an Ordinary Member of this Committee in 1917. This Committee is aiming to compile the catalogue of scientific literature published in Japan for the sake of the International Catalogue of Scientific Literature, originated by the Royal Society of London and administered by an International Council, commencing with literature of the year 1901. Although the work of this Committee was suspended in 1922, as the publication of the International Catalogue was temporarily stopped with the 14th issue owing to the

World War, the Japanese Committee is continued nominally even to the present time. In this relation, Professor Matsubara represented the Imperial Government at the Second International Convention of the International Scientific Catalogue held in London in 1905.

In 1923, Professor Matsubara was nominated by the Cabinet a Member of the National Research Council. This Council is an organization attached to the Ministry of Education and has been established in 1920 for the purpose of coordinating and encouraging activities at home in the various branches of science and its applications and also of cooperating with like institutions in other countries, with the view of promoting national and international researches in these fields, as the outcome of the conference of the representatives of the principal inter-allied Scientific Academies held in London and Paris in October and November of 1918, and the Constitutive Assembly of the International Research Council held in Brussels in July of 1919. Professor Matsubara, who was attached to the Division of Chemistry, was elected the Vice-Chairman of that Division in 1924, and the Chairman in 1930, and as such is also a member of the Division of General Affairs since 1924, besides the Chairman of the Publication Committee of this central Division and also that of the Division of Chemistry. In this connection he represented the National Research Council of Japan at the Extraordinary General Assembly of the International Research Council held in Brussels in June of 1926. This is the meeting at which it was resolved, after agreeing unanimously to omit from the Statutes of the International Council the words which have limited the membership of the Council to the allied and neutral countries, to invite Germany, Austria, Hungary and Bulgaria to join the International Research Council and the Unions attached to it. He represented the National Research Council of Japan also at the Seventh International Chemical Conference of the International Union of Pure and Applied Chemistry, held in Washington, September, 1926. As a Member of the National Research Council, he acted as General Secretary, together with the late Professor N. Yamasaki, for the Third Pan-Pacific Science Congress, held in Tokyo, October and November, 1926, under the auspices of the National Research Council of Japan.

Perhaps it may be added here that Professor Matsubara represented the Imperial Government at the Sixth International Congress of Applied Chemistry, held in Rome, April and May, 1906. He was one of the organizers of the Japanese Committee of the Pasteur Centenary Celebrations of 1922, and also of the Berthelot Centenary Celebrations of 1927, and gave memorial lectures in both of these occasions. He was also a member of several committees for the organization of the World Engineering Congress, held in Tokyo, October and November, 1929.

There is a Committee attached to the Ministry of Education for giving certificates for the teachers. Formerly the certificates for the teachers in secondary education only were concerned by this Committee. Professor Matsubara, after serving as an Examining Member of chemistry in 1907, 1910, 1911 and 1912, was appointed in 1913, by the Cabinet, one of the Standing Members of this Committee, to conduct all business connected with the testing of the qualifications of teachers for licenses, both by examination and without examination. When, in 1919, the certificates for the teachers of the Higher Courses of the Higher Schools, which are practically the preparatory courses for the universities and colleges, were determined to be given and to be controlled by this Committee, he was requested to act in the same capacity also for this section. He is still continuing to serve in both of these sections.

When School Books Investigation Committee was reorganized in 1920, Professor Matsubara was nominated, by the Cabinet, one of its Members. This Committee has to examine the textbooks for elementary schools, which relate to morals, Japanese language, arithmetic, Japanese history, geography, science, etc. Such textbooks are to be those for which the copyright is held by the State, and they are submitted to this Committee by the Minister of Education before their publication.

When, in 1907, Mr. (now Baron) Toranosuke Furukawa offered a sum of money to build a College of Science in Sendai, the Ministry of Education determined to establish the Tohoku Imperial University with this College of Science in Sendai and the College of Agriculture in Sapporo as its constituent colleges, and Professor Matsubara was nominated, by the Minister, a member of the Organization Committee of this College, which was opened in 1911.

Again, in 1927, the Post-Graduate Courses of the Higher Normal Schools of Tokyo and Hiroshima were to be reorganized each to a College of Literature and Science, according to a resolution of the Education Council passed in 1922, and Professor Matsubara was requested, by the Minister of Education, to be a member of the Organization Committee of these Colleges, which were opened in 1929.

When in 1921, the syllabus of "science" to be taught in the Literature Section of the Higher Courses of Higher Schools was to be discussed and fixed, the Ministry of Education requested Professor Matsubara to be a member of the drafting committee. Again in 1926, he acted in the same capacity when the syllabus of chemistry to be taught in the Science Section of the Higher Courses of Higher Schools was discussed and fixed. In 1924, when the syllabus of physics and chemistry to be taught in Middle Schools was revised, he also served in the revising committee.

From 1919 to 1931, Professor Matsubara acted as a consultant to the Naval Arsenal at Hiratsuka. He was a Councillor of the Institute of Physical and Chemical Research from 1930 to 1933, while he was the Dean of the Faculty of Science of the Imperial University of Tokyo. He acted as a Juror at the Tokyo Taisho Exhibition of 1914.

Professor Matsubara joined this Society, then the Tokyo Chemical Society, in 1894 as an Associate, and in 1896 as a Member. He was elected Editor of the Journal of the Society in 1899-1903, Member of the Council 1906-1907, Secretary 1907-1908, Editor 1908-1919, President 1919-1920, and Editor 1920-1926. Besides, he served on several committees of the Society, and was the centre of its activities for many years.

He joined the Society of Chemical Industry, of Japan, in 1898, and the Association of Chemical Industry, of Japan, in 1917, just after the establishment of both, and served in the Council of both of these institutions several times.

In 1908, he joined the Kogakukai (Society for the Promotion of Science), a society of some fifty people, publishing the Toyo-gakugei-zasshi (Oriental Journal of Science), a journal in the line of the "Nature" of London or the "Science" of New York, and acted as its editing secretary from 1911 to 1921.

Professor Matsubara was distinguished, through his whole course of education, by high standard of scholarship. One who ever knows him cannot help admiring his excellent memory and extreme carefulness in all details. His omnivorous stock of knowledge, and plain and impartial character made him a man who cannot be missed in all organizations in which he played always an important rôle. Indeed his meritorous and implicit contributions to the progress of sciences in Japan shall never be forgotten.

On the occasion of his retirement from the Professorship, his friends and pupils raised a considerable sum of money, which was transferred to the Chemical Society of Japan. The Society decided with gratitude to establish a fund to be used for the encouragement of the progress of chemistry, in association with the name of Professor Matsubara.

Yuji SHIBATA.

June, 1933.

BULLETIN OF THE
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THE STICK ANTIMONY ELECTRODE FOR THE MEASUREMENT OF HYDROGEN ION CONCENTRATION[1].

By Taku UEMURA and Hideo SUEDA.

Received November 12th, 1932. Published January 28th, 1933.

The usual hydrogen electrode method is undoubtedly the most accurate one of all the electrometric ways of estimating hydrogen ion concentration, but it cannot be applied to solutions containing reducible substances like ammine complex salts. We have already studied the above solution by using the quinhydrone electrode, but even in the limited range of its applications, our purpose was not attained. And, metal electrodes can be presented to these very reducible solutions for the determination of hydrogen ion concentration (pH). Several types of antimony electrode are thus reported for this purpose: Plated type, by Shukov and Aveyevich[2], and Dropping type, by Roberts and Fenwick[3], Franke and William[4], Snyder[5], Vlès and Vellinger[6], Itano[7], Parks and Beard[8] are the principal investigators on the stick antimony electrode which has been favored because of its ease of preparation and use.

The experimental formulas given by these authors have a tolerable accuracy in their own studies, but it is difficult to find the uniformity in their results. When one wishes to determine pH values by using the antimony electrode, one must fully calibrate the metal electrode. Supposing that the disagreement of data is due to the different nature and treatment of the electrode, we have paid attention to the manipulation of the metal and principally adopted Vlès-Vellinger's idea of experiments.

(1) Read before the 8th Annual Meeting of the Japanese Association for the Advancement of Science (Nippon Gakujutsu-Kyôkai), held at Nagoya, Japan, October 16th, 1932.

(2) Shukov and Aveyevich, *Z. Elektrochem.*, **35** (1929), 349; **37** (1931), 771.

(3) Roberts and Fenwick, *J. Am. Chem. Soc.*, **50** (1928), 2125.

(4) Franke and William, *Ind. Eng. Chem.*, **20** (1928), 87.

(5) Snyder, *Soil Science*, **26** (1928), 107.

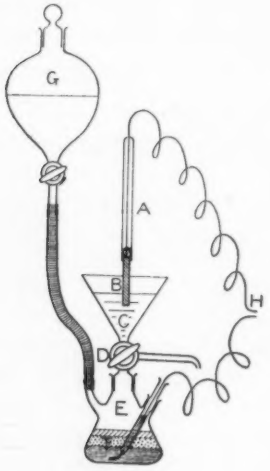
(6) Vlès and Vellinger, *Arch. phys. biol.*, **6** (1927), 38 and 92.

(7) Itano, *Ber. Ohara Inst. landw. Forsch. Japan*, **4** (1929), 273.

(8) Parks and Beard, *J. Am. Chem. Soc.*, **54** (1932), 856.

Experimental.

Apparatus. For the present determination of pH values, we have used the mode of glass vessel presented by Vlès and Vellinger[6].



A : Glass tube for protecting the antimony electrode.
B : Antimony electrode.
C : Sample for determing pH value.
D : Three way stopcock.
E : Saturated potassium chloride solution.
F : Calomel electrode.
G : Reservoir for potassium chloride solution.
H : To potentiometer.

Fig. 1.

Dimension: Diameter of glass funnel..... 6 cm.
Height of glass funnel..... 6 cm.
Diameter of glass vessel (bottom)..... 5.5 cm.

Preparation of the Stick Antimony Electrode. A hard glass tube (about 7 mm. in inside diameter and 30 cm. in length) is filled with metallic antimony pieces to occupy at first from 10 to 15 cm. in length; and, held horizontally it is gently heated on a fish-tail formed Bunsen burner. When the antimony is sufficiently fused, the tube must be slowly moved to and fro to expel the air-bubbles in the metal. Next, the red-heated glass tube containing the fused antimony is drawn to keep a uniform diameter of about 4–5 mm., and is thrown into water for sudden cooling. If cooled gradually, in this case, the solidified antimony easily gets a cleavage surface along its cross section of the stick and becomes very brittle. To connect a copper wire with the prepared antimony stick, we apply direct electric current (70 volts; 2–3 amperes), taking the wire as cathode and the metal, as anode. We thus make an arc between the electrodes, and when the end of the stick is sufficiently

fused the wire is strongly put into the fused stick of antimony. As the joint of these two metals falls easily apart, even after it was completely cooled, we generally cover the electrode with a glass tube and its end is sometimes sealed with paraffine, de Khotinsky cement or bakelite varnish.

Different Treatments of Antimony Electrodes. According to the Vlès-Vellinger's publications[6], the antimony electrode is influenced by different treatments, such as polishing with emery paper of various degrees. To study these effects more minutely, we have chosen several samples of electrodes variously prepared.

A-electrode: Compact surface polished with No. 0000 emery paper.
B-electrode: Compact surface polished with No. 00 emery paper.
C-electrode: Surface not compact, (air-bubbles are leaving mark on the surface) polished with No. 00 emery paper.
D-electrode: A-electrode containing a minute quantity of copper[9].
E-electrode: B-electrode containing a minute quantity of copper[9].
F-electrode: Polish with No. 00 emery paper and take the electrode as anode (platinum as cathode) and electrolyse water (acidified with a very small quantity of dilute sulphuric acid) from 2 to 3 minutes. Gray coloured.

All these electrodes, once polished, are again cleaned in distilled water, wiped with absorbent cotton and used.

Original Impurities detected in Antimony Pieces. We have used two kinds of antimony pieces for our present studies; one is of Japanese origin (labelled Kojima's Deer brand—Extra pure, Tokyo). By an application of the electric arc spectral method, we have detected some lines of foreign elements, thus:

Arsenic: 2349.88 Å, 2898.86 Å, 3860.60 Å
Copper: 4022.88 Å, 4062.91 Å
Lead: 3639.72 Å, 3683.62 Å
Tin: 3034.25 Å, 3175.16 Å, 3262.50 Å

Our second sample used for the preparation of the following two electrodes is the Merck's reagent where any lines of impurities can not be found, except those of arsenic.

a-electrode: Compact surface polished with No. 0000 emery paper, and left in water for more than one hour.
b-electrode: Compact surface polished with No. 0000 emery paper.

(9) About 0.1–0.01% of copper.

Buffer Solutions. We have prepared the folowing buffer solutions, whose pH values are defined by hydrogen electrode, to observe the accuracy of our stick antimony electrode.

pH
1.25 (50 c.c. M/5 KCl; 64.5 c.c. M/5 HCl, dilute to 200 c.c.)
1.96 (50 c.c. M/5 KCl; 10.6 c.c. M/5 HCl, dilute to 200 c.c.)
2.97 (50 c.c. M/5 KH Phthalate; 20.32 c.c. M/5 HCl, dilute to 200 c.c.)
3.97 (50 c.c. M/5 KH Phthalate; 0.40 c.c. M/5 NaOH, dilute to 200 c.c.)
4.99 (50 c.c. M/5 KH Phthalate; 23.85 c.c. M/5 NaOH, dilute to 200 c.c.)
6.05 (50 c.c. M/5 NaH_2PO_4; 5.70 c.c. M/5 NaOH, dilute to 200 c.c.)
7.07 (50 c.c. M/5 NaH_2PO_4; 29.63 c.c. M/5 NaOH, dilute to 200 c.c.)
7.99 (50 c.c. M/5 H_3BO_3, M/5 KCl; 3.97 c.c. M/5 NaOH, dilute to 200 c.c.)
9.00 (50 c.c. M/5 H_3BO_3, M/5 KCl; 21.30 c.c. M/5 NaOH, dilute to 200 c.c.)
9.99 (50 c.c. M/5 NaH_2PO_4; 46.80 c.c. M/5 NaOH, dilute to 200 c.c.)
10.59[10](100 c.c. Glycocoll solution[11]; 50 c.c. M/5 NaOH, dilute to 200 c.c.)
12.39[10](80 c.c. Glycocoll solution[11]; 60 c.c. M/5 NaOH, dilute to 200 c.c.)

The above mentioned buffer solutions are chosen in every one pH range and the chemicals used for the preparation have nearly the purity of reagents of the Kahlbaum's grade.

The Measured Electromotive Force (E.M.F.) Values. Table 1 shows that A- and B-electrodes, and D- and E-electrodes have respectively similar values while C- and F-electrodes show slightly different results from those of the former two pairs.

TABLE 1.

pH	Electrodes (Japanese origin)					
	A-	B-	C-	D-	E-	F-
1.25	65.3	67.7	73.0	66.0	65.8	63.2
1.96	106.7	105.5	107.5	105.7	105.5	108.4
2.97	162.5	161.6	161.6	158.5	159.5	158.9
3.97	212.2	211.3	212.8	211.6	212.8	210.6
4.99	267.9	268.5	269.1	266.9	267.7	266.7
6.05	329.6	329.6	330.9	329.8	328.0	326.8
7.07	383.4	382.0	383.7	382.7	383.0	382.1
7.99	428.3	428.1	430.6	427.6	427.8	427.1
9.00	473.9	474.9	476.5	476.5	476.7	475.4
9.99	524.3	522.8	525.6	524.4	525.9	525.7
10.59	557.0	556.0	557.6	557.5	556.5	555.9
12.39	687.0	687.1	694.7	686.0	687.1	682.6

(10) The last two solutions are mixed according to the Sörensen's indication, while the others are based on Clark and Lubs' standards.

(11) Our glycocoll (glycine) solution is prepared by dissolving 1.501 gr. glycocoll and 1.71 gr. NaCl in 200 c.c. H_2O.

Now, A- and B-electrodes, which have almost the same surface condition, have received a different mechanical treatment, and D- and E-electrades are also polished with emery paper of different degrees, but to each is added a small and equal quantity of copper. And, the result given by these two pairs of electrodes shows that any mechanical treatment influences but slightly the E.M.F. values, while the surface condition and the chemical nature of the electrodes cannot be neglected for the measurement of E.M.F.

Our second results obtained from the electrodes prepared by the Merck's reagent are as follows:

TABLE 2.

pH	Electrodes		pH	Electrodes	
	a–	b–		a–	b–
1.25	79.8	80.5	7.03	403.4	404.7
1.99	112.1	112.1	7.93	435.8	438.0
2.99	159.0	159.2	8.91	492.5	491.3
3.97	223.3	223.3	10.05	553.4	552.4
4.99	283.0	283.3	10.77	595.3	591.8
5.95	339.8	335.0	11.97	693.5	697.9

Table 2 also shows that the slight difference of mechanical treatment has very little effect on the E.M.F. values.

Next, we have found the mean of observed values that nearly coincide with each other and have tabulated them in Table 3, comparing the calculated values from our empirical equation (see page 6–7) deduced from the experimental results.

TABLE 3.

pH	Mean values of				pH	Mean values of	
	A–B (obs.)	A–B (calc.)	D–E (obs.)	D–E (calc.)		a–b (obs.)	a–b (calc.)
1.25	66.5	66.6	65.9	65.4	1.25	80.2	71.8
1.96	106.1	104.8	105.6	103.8	1.99	112.1	113.2
2.97	161.9	159.1	159.0	158.2	2.99	159.1	169.2
3.97	211.8	212.9	212.2	212.2	3.97	223.3	224.1
4.99	268.3	267.8	267.3	267.3	4.99	283.2	281.2
6.05	329.6	324.7	328.9	324.6	5.95	337.4	335.0
7.07	382.7	379.7	382.9	379.7	7.03	404.0	395.5
7.99	428.2	429.2	427.7	429.3	7.93	436.9	445.9
9.00	474.4	483.5	476.6	483.9	8.91	491.9	500.8
9.99	523.6	536.8	525.2	537.3	10.05	552.9	564.6
10.59	556.5	569.0	557.0	569.8	10.77	593.6	604.9
12.39	687.1	665.9	686.9	666.9	11.97	695.7	672.1

Theoretical.

Many authors[12] mention the theoretical side of the antimony electrode, and some of them declare that chemical changes occur on the surface of the metallic electrode, and they even give several constitutional formulas of intermediates which are supposed to be obtained. Assuming any metallic oxide whose solubility is very small, the next equation will be formed in the solution, and it shows that the metallic ion concentration of the solution is controlled by its hydrogen ion concentration.

$$MO + 2H^+ \rightleftarrows M^{++} + H_2O$$

M is, in this case, a divalent metal whose oxide is therefore MO. Supposing MO nearly insoluble, then we may have

$$[M^{++}] = K[H^+]^2 .$$

Applying the Nernst equation,

$$E = e_0 + \frac{0.0577}{2} \log [M^{++}]$$

Putting $K\ [H^+]^2$ in place of $[M^{++}]$,

$$E = e_0 + \frac{0.0577}{2}(\log K + \log [H^+]^2) ,$$

$$E = e_0' + 0.0577 \log [H^+] ,$$

$$E = e_0' - 0.0577\ \mathrm{pH} \quad (\text{at } 17^\circ\mathrm{C}) .$$

From this, we conclude that the electrode potential (E) can be varied according to pH value. It goes without saying that this conclusion holds only when the small solubility of the metallic oxide is realised, and the equation is similarly derived in the case of a trivalent metallic oxide of very small solubility. One of the few metals that fulfill these conditions is antimony.

Applying the principle of least-square method, we have derived the following empirical equations from each set of the experiments whose data of E.M.F. have already been tabulated.

(1) Equation derived from the mean values of A- and B-electrodes (see Table 3) ;

$$E = 53.8\ \mathrm{pH} - 0.7 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

(12) loc. cit.

(2) Equation derived from the mean values of D- and E-electrodes (see Table 3);

$$E = 54.0\,\mathrm{pH} - 2.1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

(3) Equation derived from C-electrode (see Table 1);

$$E = 54.0\,\mathrm{pH} + 0.3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

(4) Equation derived from F-electrode (see Table 1);

$$E = 53.8\,\mathrm{pH} - 1.8 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

(5) Equation derived from the mean values of a- and b-electrodes (see Table 3);

$$E = 56.8\,\mathrm{pH} + 1.8 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

With the theoretical values calculated from these empirical formulas and the observed results, we can make a diagram that represents the relation of pH and E.M.F. Of the two straight lines in the following

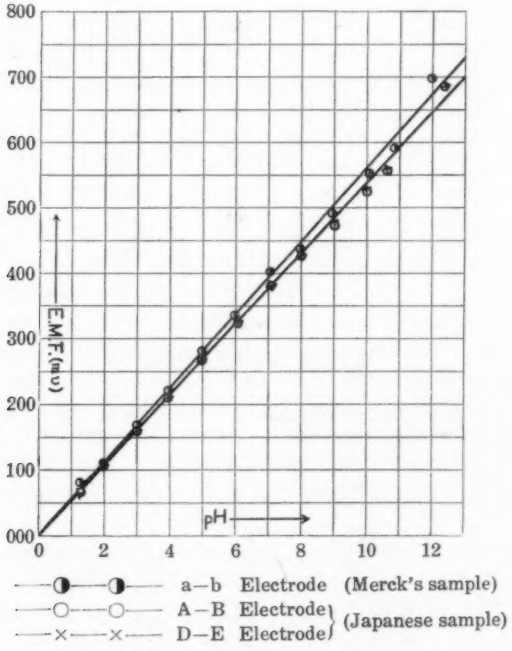


Fig. 2.

diagram (Fig. 2), the upper one shows the theoretical values deduced from the equation (5), obtained from the electrode of Merck's sample; the lower one shows the equations (1) and (2).

Next, in Tables 4 and 5, we give the maximum deviation of observed and calculated values of E.M.F. which are obtained from equations (1), (2) and (5); a percentage of the error, and the difference due to the determination of pH by hydrogen and antimony electrodes.

TABLE 4.

A-, B-, D- and E-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)		% of error from calc. value		pH—diff. (Sb to H_2)	
	A-; B-	D-; E-	A-; B-	D-; E-	A-; B-	D-; E-
1.25	−1.3	+0.6	2.0	0.9	0.02	0.01
1.96	+1.9	+1.9	1.8	1.8	0.04	0.04
2.97	+3.4	+1.3	2.1	0.8	0.06	0.02
3.97	−1.6	±0.6	0.8	0.3	0.03	0.01
4.99	+0.7	±0.4	0.3	0.2	0.01	0.01
6.05	+3.9	+4.2	1.2	1.3	0.07	0.08
7.07	+3.7	+3.3	1.0	0.9	0.07	0.06
7.99	−1.1	−1.7	0.3	0.4	0.02	0.03
9.00	−9.6	−7.4	2.0	1.5	0.18	0.14
9.99	−14.0	−12.9	2.6	2.4	0.26	0.24
10.59	−13.0	−13.3	2.3	2.3	0.24	0.25
12.39	+21.2	+20.2	3.2	3.0	0.39	0.37

TABLE 5.

a- and b-Electrodes.

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H_2)
1.25	+8.7	12.1	0.15
1.99	−1.1	1.0	0.02
2.99	−10.2	6.0	0.18
3.97	−0.8	0.4	0.01
4.99	+2.1	0.8	0.04
5.95	+4.8	1.4	0.09
7.03	+9.2	2.3	0.16

Table 5.—(*Continued*)

pH	Max. dev. of E.M.F. from calc. value (m.v.)	% of error from calc. value	pH—diff. (Sb to H_2)
7.93	−10.1	2.2	0.18
8.91	−9.5	1.9	0.17
10.05	−12.2	2.2	0.22
10.77	−13.1	2.2	0.23
11.97	+25.8	3.8	0.46

Part of the expenses of this study is defrayed with the Research Fund of the University, for which we desire to tender our gratefulness.

Summary.

As we have performed various kinds of experiments with the stick antimony electrode, changing their conditions of electrodes and external influences, we may summarise the results of our observations.

(1) The stick antimony electrode in an unstirred solution in contact with air at equilibrium gives a reliable measurement of pH values from pH 1 to 9 inclusive. Recognizing some decrease of accuracy in the results, we may of course apply this electrode for the determination of pH values above pH 9, up to 12.

(2) The value of E.M.F. (m.v.) with the electrode prepared by a Japanese sample and measured against the saturated calomel electrode is obtained by the equation $E = 53.8\ \mathrm{pH} - 0.7$.

(3) We did not take the temperature as a calculating factor, but we always record it during our observation, and we know that E.M.F. value becomes invariably greater when the temperature rises. All our experiments have been made with a temperature varying between 10°C. and 25°C., and the mean error due to the temperature gradient, in this case, is, on an average, about 4%, which is comparable to other experimental errors easily inserted in the estimation of the hydrogen ion concentration.

(4) The surface of a polished antimony electrode is probably covered in a solution with an oxide whose colour is dependent on the pH value of the solution, and the change is more striking when the solution is more acidic. When the pH value of the solution is 1 to 8, the surface of the electrode immersed in the solution becomes black, but if the

solution is alkaline (pH is 9 to 12), the immersed part shows a whitish shade of colouring.

(5) When pH is small, i.e. acidic, we generally obtain a higher value of E.M.F. at the beginning of the experiment, and the value decreases and tends to a point of equilibrium; but the opposite takes place in the case of an alkaline solution whose pH is great. We may think that colour change on the surface of the electrode immersed in a solution has perhaps some relation to this transformation of the direction of E.M.F.

(6) The time to reach equilibrium is also dependent on the pH value of the solution. It is comparatively short when the solution is slightly alkaline and its pH value is about 8 to 9, and the colour on the surface of the electrode due to the immersion cannot easily be found in this range of pH. But when the solution is strongly acidic (small pH) or strongly alkaline (large pH), the surface of the electrode changes readily in colour, and the time to reach equilibrium becomes longer.

(7) As for the effect of stirring a solution, E.M.F. deviates to a higher side after it has once reached equilibrium. If we stir the solution from the beginning of the experiment (continuous stirring), E.M.F. thus obtained gives generally a higher value than it is unstirred but when we stop the vibration, E.M.F. value decreases.

(8) Mechanical treatment by the preparation of the stick antimony electrode (Ex. emery paper for polishing) is rather little influenced for obtaining the E.M.F. value, but the original minute impurities contained in an electrode, and the porousness of the electrode cannot be neglected in the determination of E.M.F.

(9) When we have once observed with a solution saturated with antimony oxide, results are obtained at equilibrium, and they are nearly similar to those of an ordinary case. We may, therefore, conclude that the chemical change of the electrode, often discussed by some authors, is not a great factor in the use of the antimony electrode.

(10) When we immersed two electrodes in the same solution but, at different times, the course followed to reach equilibrium are nearly parallel. If the equilibrium is once established by an electrode in a given solution, and we only change the electrode with a polished one, or use the same after polished it again, nearly the same course taken in the first case may also be followed to obtain an equilibrium value.

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RHYTHMIC PRECIPITATES.

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In the experiments on the diffusion of electrolytes in jellies, the author has found some new examples of rhythmic precipitates. In this communication the obtained results is reported briefly. The formations of rhythmic precipitates have been observed in the following cases: oxalates of calcium and strontium, copper hydroxide, and lead chromate in silica gel, and silver chromate in gelatine gel. The last mentioned case is, of course, the best known example of the rhythmic precipitate, yet it is described here because the author succeeded in making more beautiful and more sharp layers of silver chromate than ever obtained.

Calcium Oxalate in Silica Gel. To 5 c.c. of sodium silicate solution (density, 1.06) add 5 c.c. of a mixture of acetic and oxalic acid solutions (0.5 N., ratio of two acids: 1:1 or 1:3). This silica gel set in one night. Now ca. 5 c.c. of calcium chloride solution (10 to 25% solution) are poured on the gel. The banding readily forms which has an appearance like the opal. Clear spaces between bands are so narrow that the banding can better be seen by the transmitted light. Too large or too small quantity of oxalic acid prevents the formation of calcium oxalate band.

Strontium Oxalate in Silica Gel. To 5 c.c. of water glass solution (1.06) add equal volume of the mixed acid above described, and 0.01 –0.02 gr. of potassium citrate. After setting the gel put 5 c.c. of 25% strontium nitrate solution on it. About a week later, the formation of the banding of strontium oxalate is found. When the solution of strontium nitrate is poured on the silica gel containing the soluble oxalate or oxalic acid only, no strata is formed. It has previously been found by Hatschek[1] that the addition of material indifferent to the reaction system often causes the formation of bands. It is moreover known that citrate of potassium or sodium accelerates the formation of nucleus of the crystals. If the jelly contains citrate the nucleus formation will be accelerated and, accordingly, the formation of strata will become easier. By adding a small quantity of potassium citrate to the mixture before setting, the author has found the formation of dense, white banding of strontium oxalate.

(1) Hatschek, *Kolloid Z.*, **27** (1920), 225; *Biochem. J.*, **14** (1920), 418.

The formation of periodic precipitate of barium oxalate in silica gel could not be observed whether the citrate was added or not. Without the addition of citrate the barium oxalate grows as beautiful dentrites or plumes. The addition of small amount of glucose gives the crystal of silky lustre and the crystals become larger. In the lower part of the test-tube grow crowds of thin long plates, composed of many needles just like asbestus, and each plate often measures more than 3–4 mm. When citrate is added in the silica gel, the dentrites or plumes are not formed but many small globules and crystals form. At the lower part of the test-tube considerably large well-defined crystals of barium oxalate are formed. It measures often 2–3 mm. long.

Copper Hydroxide in Silica Gel. To 5.5–6 c.c. of sodium silicate solution add 5 c.c. of 0.5 N. acetic acid. After setting the basic gel put 0.5 N. copper sulphate solution as outer electrolyte. Two or three large thick bluish white layers are formed. Besides, in the lower part of the test-tube faint layers are also formed. These precipitates are probably copper hydroxide. Fig. 1 is the photograph of it.(2)

Copper hydroxide in silica gel
Fig. 1.

Lead chromate in silica gel
Fig. 2.

Silver chromate in gelatine gel
Fig. 3.

(2) The photographs were kindly taken by Mr. N. Asada, for which the writer expresses his hearty thanks.

Lead Chromate in Silica Gel. In 5 c.c. of sodium silicate solution dissolve 0.01–0.005 gr. of potassium chromate as inner electrolyte and 0.03–0.05 gr. of glucose. To this solution add an equal volume of a half normal solution of acetic acid. After setting 10% lead nitrate solution is poured on the gel as outer electrolyte. Ten or more days later, we find that many thin and crowded bands were formed. If too much potassium chromate are added, the dentrites are also formed simultaneously, and if too little, the bands become very vague.

It is said that lead chromate precipitates in bands in agar-agar gel but not in gelatine and in silica gel. In the author's experiment, however, the periodicity has also been observed in silica gel. In the periodic precipitates of mercuric iodide in silica gel H. N. Holmes[3] has found that the presence of glucose in the gel makes the bands very much sharper. In the same manner, the author has found that the addition of glucose makes the periodic structure of the lead chromate much sharper. In this case, two periodicities exist just as the case of silver chromate banding in gelatine containing small amount of soluble chlorides. Larger periodicity is easily recognised while smaller one is often difficultly observable without using a magnifying glass. At the lower part of the tube, however, both can easily be recognised with the naked eyes. It is interesting that in this case the upper part of the jelly is coloured yellow, the subsequent layer orange and the lower brown. Under this part the banding appears and the lowermost part becomes yellow again. It seems that such colour change is caused by the size of crystals formed. The photograph is shown in Fig. 2.

Silver Chromate in Gelatine Gel. Banding of silver chromate in gelatine gel was first found by R. E. Liesegang[4] and since then, many papers have been published on this subject. It is known that silver chromate does not deposit in bands in pure agar-agar gel, while S. C. Bradford[5] succeeded in making bands in agar gel by addition of small amount of potassium citrate. According to Bradford, the existence of salts of polyvalent acids such as citrates increases, generally, the metastable limit of crystallization of silver chromate or dichromate, and accordingly, the deposited crystals will be smaller in size. And this condition favors the formation of banding.

In the case of gelatine jelly, the banding appears without the addition of any indifferent substance, though the formed silver chromate is

(3) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 803.
(4) Liesegang, *Naturwiss. Wochenschr.*, **11** (1896), 353.
(5) See, Alexander, "Colloid Chemistry," Vol. I (1926), p. 790.

fairly coarse. So, for the same reason, if citrate is added in the inner electrolyte, more beautiful and sharper layers of very fine crystals may be expected. The experiment has been conducted as follows.

Let 0.2 gr. of gelatine swell in 10 c.c. of water and then dissolve by warming on a water bath and filter, if necessary. Then add 0.01 gr. of potassium dichromate and 0.02 gr. of potassium citrate. After setting completely, 5 c.c. of 15% silver nitrate solution are poured on the gel and stand it in a dark cold place. The banding is obtained which is more beautiful and sharper than usual (Fig. 3).

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STUDIES ON PUTREFACTIVE PRODUCTS OF BEER YEAST.

By Kôtaro NISHIDA.

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Formerly, as putrefactive products of yeast, ethylamine, trimethylamine, isoamylamine, caprylamine and sepsin were isolated by Hesse,[1] Müller[2] and Faust[3]; and recently the writer[4] reported with Dr. Yoshimura on the occurrence of hypoxanthine, histamine, putrescine, cadaverine, tyramine and leucine in a putrefied yeast. In this experiment, the author isolated the phenylethylamine, adenine, hypoxanthine, histamine, putrescine, cadaverine, tyramine and leucine from putrefied beer yeast.

Experimental Part.

The beer yeast experimented was obtained by pressing and drying the settled yeast in the bottom of fermenting tunk after main-fermentation of beer; and the various forms of nitrogen in the dried sample were as follows:

(1) Hesse, *Jahresber. Fortschr. Chem.*, (1857) 403.
(2) Müller, *J. prakt. Chem.*, **70** (1859), 65.
(3) Faust, *Arschiv. exper. Path. Pharm.*, **51** (1904), 248.
(4) K. Yoshimura and K. Nishida, *J. Agr. Chem. Soc. Japan*, **8** (1932), 309.

	Moisture 9.64%	Dry matter 90.36%
	In 100 parts of dry matte	Ratio (Total N as 100)
Total N	10.153	100.0
Protein N	6.883	67.8
Non-protein N	3.270	32.2
In which:		
Ammonia N	0.097	1.0
Organic base N	1.481	14.6
Other N	1.692	16.6

In earthen pot, 9 kg. of the sample were allowed to stand in 36 liters of water for 28 days, stirring the mixture one time in every day. In this period, average of maximum temperature daily was 28.3°C., average of minimum temperature 10.0°C., and average of temperature at 10 a.m. daily 22.5°C. In the above conditions the putrefaction took place, and still the liquid was kept an acidic reaction.

The various forms of nitrogen in the filtrate of the putrefied substance were determined:

	In 100 parts of original sample	Ratio (Total N as 100)
Total N	8.277	100.0
Protein N	0.625	7.6
Non-protein N	7.652	92.4
In which:		
Ammonia N	1.192	14.4
Organic base N	2.370	28.6
Other N	4.090	49.4

Isolation and Identification of Organic Bases. To remove protein and other impurities, neutral- and basic-lead acetate were added to the above putrefied yeast; when the excess of lead was removed by sulphuric acid and the mother liquor from the lead sulphate was evaporated to a small volume, the considerable amounts of inorganic substances (ammonium- and potassium-sulphate) crystallised out. The filtrate from the preceding inorganic substances was diluted with 5% sulphuric acid, and then researches were carried out on the organic bases, fractionally precipitated by adding phosphotungstic acid to the above solution.

First Precipitate by Phosphotungstic Acid.

This precipitate was decomposed by baryta, and excess of baryta was removed by CO_2 and the solution was fractionated into five fractions.

I. Volatile Base (Phenylethylamine). The diluted solution of free bases obtained by the above treatment was distilled under reduced pressure, and the distillate was received into dilute hydrochloric acid, and then the alcohol soluble base was isolated as hydrochloride. The yield was 2.90 gr. The hydrochloride formed colourless thin plates of silky lustre, and melted at 215–216°C. (uncorr.). Its analytical results agreed with the hydrochloride of the compound having the formula $C_8H_{11}N$.

No.	Subst. mg.	CO_2 mg.	H_2O mg.	C%	H%	N%	Cl%
(1)	3.261	7.270	2.350	60.80	8.06	—	—
(2)	3.854	8.620	2.807	61.00	8.15	—	—
(3)	4.545	0.335 c.c. N(22.5°C., 761. 8 mm.)				8.53	—
(4)	6.245	0.461 c.c. N(22.5°C., 761. 2 mm.)				8.54	—
(5)	4.780	4.245 mg. AgCl		—	—	—	21.98
(6)	6.720	5.970 mg. AgCl		—	—	—	21.98
Calc. for $C_8H_{11}N$·HCl				60.93	7.68	8.89	22.50

The chloroaurate, readily soluble in water and alcohol, crystallised in yellow thin plates of pearly lustre.

Anal. : Subst. = 0.1088, 0.2470, 0.4952; Au = 0.0468, 0.1059, 0.2115 gr.
Found : Au = 43.01, 42.87, 42.71%.
Calc. for $C_8H_{11}N$·HCl·$AuCl_3$ (Phenylethylamine chloroaurate): Au = 42.76%.

The chloroplatinate of the base, hardly soluble in water and alcohol, crystallised in small bright golden yellow prisms and melted at 247–248°C. (uncorr.) with decomposition.

Anal. : Subst. = 0.2156, 0.1523, 0.0498; Pt = 0.0645, 0.0452, 0.0148 gr.
Found : Pt = 29.92, 29.68, 29.72%.
Calc. for $(C_8H_{11}N\cdot HCl)_2$ $PtCl_4$ (Phenylethylamine chloroplatinate): Pt. = 29.94%.

The hydrochloride was converted into picrate by adding Na-picrate to its aqueous solution. It formed yellow prisms and melted at 170°C. (uncorr.). From these results, the volatile organic base obtained from the putrefied yeast is no doubt phenylethylamine.

II. The Base Crystallised out as Nitrate (Adenine). The residual solution after the distillation of volatile base was slightly acidified with nitric acid and by evaporation of the solution 11.50 gr. of adenine nitrate were crystallised out. Analytical results of the nitrate are as follows.

Anal.: Subst. = 0.2348; H_2O = 0.0111 gr.
Subst. = 0.2491; Nitron nitrate = 0.4477 gr.
Found: H_2O = 4.73%; HNO_3 = 30.19%.
Calc. for $C_5H_5N_5 \cdot HNO_3 \cdot \frac{1}{2}H_2O$ (Adenine nitrate): H_2O = 4.35%; HNO_3 = 30.43%.

The picrate of characteristic hairly needles is yellow and sparingly soluble in water and it decomposes at 282°C. (uncorr.).

The chloroaurate, which was converted from the picrate, crystallised in yellow prisms and melted at 263°C. (uncorr.).

Anal.: Subst. = 0.1067, 0.0723; Au = 0.0505, 0·0341 gr.
Found: Au = 47.33, 47.16%.
Calc. for $C_5H_5N_5 \cdot 2HCl \cdot 2AuCl_3 \cdot H_2O$ (Adenine chloroaurate): Au = 47.35%.

III. Precipitate by Silver Nitrate (Hypoxanthine). The precipitate by silver nitrate was decomposed by hydrochloric acid. When the filtrate from AgCl was evaporated under reduced pressure, crystals of the hydrochloride of the base (13.70 gr.) separated out. Its chloroaurate forms yellow prisms and decomposes at 246–247°C. (uncorr.).

Anal.: Subst. = 0.3015; Au = 0.1246 gr. Found: Au = 41.33%.
Calc. for $C_5H_4N_4O \cdot HCl \cdot AuCl_3$ (Hypoxanthine chloroaurate): Au = 41.42%.

The hydrochloride was also analysed as its chloroplatinate.

Anal.: Subst. = 0.2309; Pt = 0.0658 gr. Found: Pt = 28.50%.
Calc. for $(C_5H_4N_4O \cdot HCl)_2 PtCl_4$ (Hypoxanthine chloroplatinate): Pt = 28.62%.

The above results agree fairly well with the data of hypoxanthine derivatives.

IV. Precipitate by Silver Nitrate and Baryta. The precipitate, prepared by silver nitrate and baryta, was treated with hydrochloric acid and sulphuric acid to remove the silver and baryta. Then phosphotungstic acid was added to the above filtrate, and the precipitate was decomposed by baryta. The filtrate from barium phosphotungstate after removing the excess of baryta by carbon dioxide was concentrated to a small volume under reduced pressure; and then hydrochloric acid was added to the solution of free base obtained by the above treatment.

The hydrochloride freed from water was treated with cold absolute alcohol and was separated as follows:

(A) *Insoluble Portion in Absolute Alcohol* (*Histamine*). From this portion 7.80 gr. of colourless hygroscopic substance were obtained, which gives intensive diazo-reaction. Its picrate formed rhombic plates of bright yellow and decomposed at 232~233°C. (uncorr.).

The chloroaurate of the base prepared from the hydrochloride crystallised in yellow prisms and decomposed at 218°C. (uncorr.).

Anal.: Subst. = 0.4131; Au = 0.2061 gr. Found: Au = 49.89%.
Calc. for $C_5H_9N_3 \cdot 2HCl \cdot 2AuCl_3$ (Histamine chloroaurate): Au = 49.85%.

(B) *Soluble Portion in Absolute Alcohol* (*Histamine*). The yield of the base from the precipitate, which was formed by adding saturated alcoholic solution of $HgCl_2$ to this portion, was 1.30 gr. as hydrochloride. The hydrochloride was hygroscopic, colourless prisms and gave intensive diazo-reaction. The natures of its picrate and chloroaurate were as follows: The picrate formed yellow rhombic crystals and decomposed at 231°C. (uncorr.). The chloroaurate of the base crystallised in golden yellow prisms and melted at 218°C. (uncorr.) with decomposition.

Anal.: Subst. = 0.2936, 0.1876; Au = 0.1464, 0.0930 gr.
Found: Au = 49.86, 49.57%.
Calc. for $C_5H_9N_3 \cdot 2HCl \cdot 2AuCl_3$ (Histamine chloroaurate): Au = 49.85%.

These results agree precisely with histamine derivative in all respects.

V. Filtrate from Silver Nitrate- and Baryta-Precipitate. The filtrate was treated with hydrochloric acid and sulphuric acid to remove an excess of silver and baryta. Then phosphotungstic acid was added to the above solution, and the precipitate obtained thus was decomposed by baryta. The filtrate from barium phosphotungstate after removing the excess of baryta by carbon dioxide was concentrated to a small volume under reduced pressure. The solution of free base obtained from the above treatment was converted into the hydrochloride by adding hydrochloric acid. And the hydrochloride freed from water was treated with cold absolute alcohol and was separated as follows:

(A) *Insoluble Portion in Absolute Alcohol* (*Tyramine*). The yield was 2.30 gr. It was colourless plates of silky lustre and gave strong Millon's reaction. The picrate formed deep yellow prisms and melted at 203°C. (uncorr.). The chloroplatinate crystallised in orange yellow,

long prisms, hardly soluble in water, decomposed at 224–225°C. (uncorr.) and remarkably gave phenol odour by ignition.

Anal.: Subst. = 0.1131, 0.0762; Pt = 0.0323, 0.0216 gr.
Found: Pt = 28.56, 28.35%.
Calc. for $(C_5H_{11}NO\cdot HCl)_2PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

These results agree well with tyramine derivatives.

(B) *Soluble Portion in Absolute Alcohol.* The alcohol soluble portion gave a white precipitate by the addition of saturated alcoholic solution of mercuric chloride.

(a) Precipitate by Mercuric Chloride (Putrescine). When the mercury was removed by sulphuretted hydrogen and the liquid freed from mercuric sulphide was evaporated to a small volume, the hydrochloride of the base was crystallised out (1.10 gr.). The picrate formed greenish yellow prisms, hardly soluble in water, and decomposed at 252–253°C. (uncorr.). The hydrochloride was also analysed as its chloroaurate (Decomp. point = 231°C.).

Anal.: Subst. = 0.3055; Au = 0.1564 gr. Found: Au = 51.19%.
Calc. for $C_4H_{12}N_2\cdot 2HCl\cdot 2AuCl_3$ (Putrescine chloroaurate): Au = 51.35%.

The chloroplatinate of the base formed glistening orange yellow prisms, and decomposed at 222–223°C. (uncorr.). The result of the analysis was as follows:

Anal.: Subst. = 0.1994; Pt = 0.0781 gr. Found: Pt = 39.17%.
Calc. for $C_4H_{12}N_2\cdot 2HCl\cdot PtCl_4$ (Putrescine chloroplatinate): Pt = 39.13%.

(b) Filtrate from $HgCl_2$-precipitate (Tyramine). The alcoholic solution filtered from the $HgCl_2$-precipitate was evaporated and the residue was suspended in water, treated with sulphuretted hydrogen gas and the mercuric sulphide was filtered off. Then the hydrochloride of the base (2.40 gr.) was obtained from the above filtrate. It was colourless thin plates of silky lustre and gave strong Millon's reaction. The picrate prepared from the hydrochloride formed yellow prisms and decomposed at 203°C. (uncorr.). The chloroplatinate of the base crystallised in orange yellow prisms and decomposed at 223–224°C. (uncorr.). It gave remarkably odour of phenol by ignition, and the amount of platinum in it was as following.

Anal: Subst. = 0.1557; Pt = 0.0438 gr. Found: Pt = 28.13%.
Calc. for $(C_5H_{11}NO\cdot HCl)_2PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

Second Precipitate by Phosphotungstic Acid.

I. Volatile Base (Phenylethylamine). Dilute solution of free bases prepared from the precipitate which was deposited by phosphotungstic acid was distilled under reduced pressure and the distillate was received into dilute hydrochloric acid, and then alcohol soluble base was separated as hydrochloride. The yield was 4.30 gr. It was colourless thin plates having silky lustre and its M.P. being 214°C. (uncorr.). The chloroaurate of the base crystallised in yellow thin plates of pearly lustre.

Anal.: Subst. = 0.1329, 0.3435, 0.4889; Au = 0.0564, 0.1470, 0.2083 gr.
Found: Au = 42.44, 42.79, 42.61%.
Calc. for $C_8H_{11}N \cdot HCl \cdot AuCl_3$ (Phenylethylamine chloroaurate): Au = 42.76%.

The chloroplatinate crystallised in golden yellow small prisms, hardly soluble in water and alcohol. It turned to black at about 230°C. and decomposed at 246–247°C. (uncorr.).

Anal.: Subst. = 0.1530, 0.2444; Pt = 0.0459, 0.0735 gr.
Found: Pt = 30.00, 30.07%.
Calc. for $(C_8H_{11}N \cdot HCl)_2PtCl_4$ (Phenylethylamine chloroplatinate): Pt = 29.94%.

II. Non-Volatile Bases. After the volatile base was removed, the concentrated residual solution was acidified with hydrochloric acid and evaporated to dryness on a water-bath. The residual mass was separated into soluble and insoluble portions by using absolute alcohol.

(A) *Insoluble Portion in Absolute Alcohol* (KCl). The amounts of this portion obtained were 19.80 gr. It was colourless short prisms and gave violet flame reaction. The analysis of its chloroaurate is as follows.

Anal.: Subst. = 0.1957; Au = 0.1019 gr. Found: Au = 52.07%.
Calc. for $KCl \cdot AuCl_3$ (Potassium chloroaurate): Au = 52.15%.

(B) *Soluble Portion in Absolute Alcohol.* The alcoholic solution filtered from the above insoluble portion was treated with the saturated alcoholic solution of mercuric chloride.

(a) Precipitate by Mercuric Chloride (Cadaverine). From the precipitate by mercuric chloride, 4.10 gr. of colourless hygroscopic crystals were obtained as hydrochloride. The picrate formed bright yellow prisms, hardly soluble in water, and melted at 223°C. (uncorr.) with decomposition. The chloroaurate crystallised in deep yellow irregular prisms and decomposed at 225°C. (uncorr.).

Anal.: Subst. = 0.4743; Au = 0.2376 gr. Found: Au = 50.09%.
Calc. for $C_5H_{14}N_2 \cdot 2HCl \cdot 2AuCl_3$ (Cadaverine chloroaurate): Au = 50.38%.

The chloroplatinate of the base formed short prisms with glistening golden yellow colour.

Anal.: Subst. = 0.1417; Pt = 0.0542 gr. Found: Pt = 38.25%.
Calc. for $C_5H_{14}N_2 \cdot 2HCl \cdot PtCl_4$ (Cadaverine chloroplatinate): Pt = 38.06%.

(b) Filtrate from Mercuric Chloride-Precipitate (Tyramine). 7.70 Gr. of hydrochloride of the base were obtained from this portion. It was colourless thin plates of silky lustre and gave intensive Millon's reaction. The picrate formed yellow prisms and decomposed at 203°C. (uncorr.). The chloroplatinate of the base was orange yellow thin plates of pearly lustre, and it decomposed at 222°C. (uncorr.) and gave a strong odour of phenol by ignition.

Anal.: Subst. = 0.1470, 0.1164; Pt = 0.0415, 0.0334 gr.
Found: Pt = 28.23, 28.69%.
Calc. for $(C_8H_{11}NO \cdot HCl)_2 \cdot PtCl_4$ (Tyramine chloroplatinate): Pt = 28.48%.

Filtrate from Phosphotungstic Acid-Precipitate. (*Leucine*).

The filtrate from the second precipitate by phosphotungstic acid was alkalified by adding the saturated solution of baryta, and the precipitates of Ba-sulphate and Ba-phosphotungstate were filtered off. Then the filtrate which was freed exactly from the excess of baryta with sulphuric acid was concentrated to a small volume and 324.90 gr. of crystals were obtained.

Anal.: Subst. = 0.1018; N = 0.01107 gr. Found: N = 10.87%.
Calc. for $C_6H_{13}NO_2$ (Leucine): N = 10.69%.

It was converted into copper salt and the content of copper was determined.

Anal.: Subst. = 0.0585, 0.0917; CuO = 0.0142, 0.0228; Cu = 0.01822, 0.01135 gr.
Found: Cu = 19.40, 19.87%.
Calc. for $(C_6H_{12}NO_2)_2Cu$ (Leucine copper): Cu = 19.64%.

In conclusion, the author wishes to express his thanks to Dr. K. Yoshimura, Director of the college, for valuable advice, and to Mr. A. Yamada for the kind assistance.

Summary.

The quantities of substances isolated from 9 kg. of the dried beer yeast by putrefaction were as follows:

Phenylethylamine (as hydrochloride)	7.20 gr.
Adenine (as nitrate)	11.50 „
Hypoxanthine (as hydrochloride)	13.70 „
Histamine (as hydrochloride)	9.10 „
Tyramine (as hydrochloride)	12.40 „
Putrescine (as hydrochloride)	1.10 „
Cadaverine (as hydrochloride)	4.10 „
Leucine	324.90 „
Ammonia	128.74 „

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November, 1932.

STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. VIII. REDUCTION OF αβ-DINAPHTHYL KETONE (AN ATTEMPT TO COMPARE THE ELECTRO-NEGATIVITIES OF α- AND β-NAPHTHYL RADICALS).

By Masao MIGITA.

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Skraup[1] has observed in his research on the affinity requirement of organic radicals, that in the two naphthyl radicals, the affinity requirement in α-position is stronger than in β-position.

In the studies on dissociation of hexa-aryl ethanes, Gomberg and his colaborators[2] have found that α-naphthyl radical is more potent than β-naphthyl radical, in causing the dissociation of the ethane-molecules, e.g. di-α-naphthyl-tetraphenyl ethane dissociates into the monomer to 68% in benzene solution, while di-β-naphthyl-tetraphenyl ethane dissociates to 32.3%. If it is admitted to take the dissociation degree of hexa-aryl ethanes for a criterion of electronegativities of substituents in their molecules[3], we can infer from these results that between α- and β-naphthyl radicals the former exceeds the latter in its electronegativity.

The author[4] has attained to the same result, infering the relative electronegativities of α- and β-naphthyl radicals indirectly from the fact

(1) Skraup, *Ber.*, **55** (1922), 1080.
(2) Gomberg, *Chem. Rev.*, **1** (1925), 104.
(3) Migita, this Bulletin, **7** (1932), 382.
(4) Migita, this Bulletin, **7** (1932), 378.

that in the rearrangement of sym. di-*p*-anisyl-di-*α*-naphthyl glycol[5], *α*-naphthyl radical migrates, though to a lesser extent, as well as *p*-anisyl radical, while in the case of sym. di-*p*-anisyl-di-*β*-naphthyl glycol, migration of *p*-anisyl radical occurs almost exclusively.

Though it is intended, in the present work, to compare the electronegativities of *α*- and *β*-naphthyl radicals directly by the pinacoline method from the rearrangement products of sym. *ααββ*-tetranaphthyl glycol, all attempts to obtain this pinacone from *αβ*-dinaphthyl ketone have proved unsuccessful.

Glacial acetic acid and zinc dust reduced this ketone to *αβ*-dinaphthyl methane at higher temperature, and to *αβ*-dinaphthyl carbinol at room temperature, as in the case of *β*-naphthyl-diphenylyl ketone[6]. The author has also proved that the similar result is obtained under the same conditions in the case of *α*-naphthyl-diphenylyl ketone. The formation of the corresponding methanes in the reduction of ketones by *zinc dust and glacial acetic acid* is considered to be rather anomalous, and the case of Michler's ketone[7] is probably the only precedent found in literature.

In this anomalous reduction, negativities of the substituents are not deemed to be the directing factor, because ketones containing more negative radicals than naphthyl are not reduced to the methanes under the same conditions, as seen in the case of di-*p*-methoxy-benzophenone[8] and *p*-methoxy-*p'*-ethoxy-benzophenone[8]. The author wishes to attribute this to the sterical influence of the substituents. The fact that Michler's ketone (I) is reduced to corresponding methane by zinc dust and acetic acid, while dimethyl-*p*-aminobenzophenone[9] (II) is reduced to corresponding pinacone, seems to throw some hints on this problem.

(I) $(CH_3)_2NC_6H_4\cdot CO\cdot C_6H_4N(CH_3)_2$, (II) $(CH_3)_2NC_6H_4\cdot CO\cdot C_6H_4NH_2$.

αβ-Dinaphthyl ketone remained unchanged by the action of absolute alcohol under direct sunlight, as in the case of *p*-anisyl-*β*-naphthyl ketone, presumably owing to its extremely small solubility in absolute alcohol.

When the ketone was reduced by magnesium and magnesium iodide, the reaction seemed to proceed for the desired direction, since evolution of heat and formation of ketyl solution with wine-colour were observed in the process of reduction. However, the reaction product was dark

(5) Bailar, *J. Am. Chem. Soc.*, **52** (1930), 3596–3603.
(6) Migita, this Bulletin, **7** (1932), 385–386.
(7) Votoček and Krauz, *Ber.*, **42** (1909), 1602.
(8) Migita, this Bulletin, **7** (1932), 335, 342.
(9) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.

coloured rosinous matter, of which purification from organic solvents was tried in vain by every means. On allowing the syrupy product to stand at room temperature for a long period, a minute quantity of granular crystals was obtained. But the yield was too poor to give a further investigation.

Experimental Part.

αβ-Dinaphthyl Ketone. This ketone was prepared after Tschitschibabin and Korjagin[10], from 30 gr. of α-bromo-naphthalene, 4 gr. of magnesium and 15 gr. of β-naphtho-nitrile. The product, purified from acetic ester, melts at 136–7°C. It dissolves in concentrated sulphuric acid with orange colour.

Reduction of αβ-Dinaphthyl Ketone.

Reduction by Zinc Dust and Glacial Acetic Acid. (a) *At Boiling Temperature.* Two grams of the ketone were reduced by boiling with 8 c.c. of glacial acetic acid and 4 gr. of zinc dust, and the reaction product was usually poured into water. The resulting precipitates contained yellowish substance which is readily soluble in organic solvents imparting the solution green fluorescence, and were found freed from it only by repeated fractional crystallisation from hot ligroin. As this impurity separates out as yellowish rosinous matter from warm ligroin solution, the crude product was dissolved in hot ligroin and the solution was decanted from the rosin after full precipitation of it, and cooled quietly. White crystalline mass which deposited on the side of beaker, was gathered and recrystallised from ether. It forms thick prisms and melts at 96°C. It was identified by this melting point and elementary analysis as αβ-dinaphthyl methane, prepared by Tschitschibabin[11] by reducing αβ-dinaphthyl carbinol with hydrogen iodide in hot glacial acetic acid.

Anal.: Subst. = 0.0712; CO_2 = 0.2440; H_2O = 0.0396 gr.
Found: C = 93.6; H = 6.24%.
Calc. for $C_{21}H_{16}$ (αβ-dinaphthyl methane): C = 94.0; H = 5.97%.

(b) *At Room Temperature.* To the solution of 2.2 gr. of the ketone dissolved in sufficient glacial acetic acid (ca. 400 c.c.) to keep it solution at room temperature, were added 10 gr. of zinc dust, and the reaction mixture was allowed to stand at room temperature for five days. The crude product, obtained after usual treatments, was found readily

(10) Tschitschibabin and Korjagin, *Chem. Centr.*, (1914), I, 1658.
(11) Tschitschibabin, *Ber.*, **44** (1911), 449.

soluble in organic solvents except ligroin and petroleum ether. It crystallises from a quantity of ligroin in fine white needles, grouped in burr-like masses, which melts at 112–3°C. to a colourless liquid[12]. It dissolves in concentrated sulphuric acid with pure blue colour. It was identified from these properties and the elementary analysis, as $\alpha\beta$-dinaphthyl carbinol, prepared by Tschitschibabin[13] from α-bromo-naphthalene and β-naphthaldehyde by Grignard's reaction. The yield was nearly quantitative.

Anal.: Subst. = 0.0684; CO_2 = 0.2219; H_2O = 0.0347 gr.
Found: C = 88.6; H = 5.70%.
Calc. for $C_{21}H_{16}O$ (αβ-dinaphthyl carbinol): C = 88.7; H = 5.64%.

Reduction by Absolute Alcohol under Direct Sunlight. Two grams of ketone and 50 c.c. of absolute alcohol were sealed in a tube and exposed to direct sunlight for about two months. Though the weather was not favourable, the net time of exposure amounted to 200 hours. During the exposure, the solution assumed brownish tint, but on opening the tube, formation of acetaldehyde was not observed and the crystals in the tube were identified as unchanged ketone which was recovered quantitatively.

Reduction by Magnesium and Magnesium Iodide. To 2 gr. of powdered magnesium, suspended in 20 c.c. ether and 30 c.c. of benzene were added 2 gr. of iodine and kept the solution boiling quite vigorously. The practically colourless solution of the magnesium iodide was cooled and to it were added 2 gr. of αβ-dinaphthyl ketone dissolved in 10 c.c. of benzene. While the reaction mixture was shaken, heat was evolved and after few hours the solution assumed wine-colour. Shaking was continued until evolution of heat ceased and magnesium was uncoated. After twenty hours, the green solution was filtered from unchanged magnesium and was hydrolysed by dilute sulphuric acid with the addition of a pinch of sodium bisulphite. The benzene solution was dehydrated with sodium sulphate and the solvent was distilled off. Brown syrupy residue was easily soluble in organic solvents and purification from various organic solvents has been tried in vain. On allowing the syrupy mass to stand for about two weeks, some crystals were deposited on the side of beaker, which dissolved in concentrated sulphuric acid with intense green colouration. However, the yield was too poor to give a further investigation.

***p*-Bromo-Diphenyl.** *p*-Bromo-diphenyl was prepared after Gomberg and Bachmann[14] by diazotizing *p*-bromo-aniline and coupling it with benzene. Purification of the crude product was, however, simplified by

(12) Tschitschibabin purified this carbinol from benzene and gave it a melting point 106–7°C. However, his sample is probably not in a reliably pure state, since benzene, in which this carbinol is rather easily soluble, is not taken for a suitable solvent for purification. The author has actually observed that the carbinol obtained by purifying the crude product from benzene, melted at 106–7°C. *to a yellow liquid*, while the product purified from ligroin melted at 112–3°C. *to a colourless liquid.*

(13) Tschitschibabin, *Ber.*, **44** (1911), 447.

(14) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46** (1924), 2339.

recrystallising it from hot ligroin with an addition of animal charcoal. It crystallises in white lamellar, melting 90–91°C. to colourless liquid, while the product purified by the original method[15], melted to slightly coloured liquid at 89–90°C.

α-Naphthyl-Diphenylyl-Ketone. This ketone was prepared from 14.4 gr. of *p*-bromo-diphenyl, 0.5 gr. of activated magnesium and 10 gr. of α-naphtho-nitrile. The resulting magnesium complex was hydrolysed and subjected to steam distillation alternately in acidic and alkaline reactions. Dark coloured product was treated with ether to remove colouring impurities, and then purified from a quantity of absolute alcohol. It crystallises in fine needles, melting at 140–141°C. It is sparingly soluble in cold organic solvents, especially in glacial acetic acid. It dissolves in concentrated sulphuric acid with reddish orange colouration. The yield of the purified product was about 3.5 gr.

Anal.: Subst. = 0.0627; CO_2 = 0.2055; H_2O = 0.0301 gr.
Found: C = 89.4; H = 5.38%.
Calc. for $C_{23}H_{16}O$ (α naphthyl-diphenylyl-ketone): C = 89.6; H = 5.19%.

α-Naphthyl-Diphenylyl-Carbinol, $(\alpha\text{-}C_{10}H_7)(C_6H_5.C_6H_4)CHOH$. One gram of α-naphthyl-diphenylyl ketone was dissolved in 300 c.c. of glacial acetic acid and was allowed to react with excess of zinc dust for four days at 25°C. The reaction mixture was treated as usual and the resulting raw product was recrystallised from ligroin. It crystallises in white microscopical prisms, melting at 131°C. to a glassy mass. It dissolves in concentrated sulphuric acid imparing the solution intense greenish blue colour. Its composition was found corresponding to carbinol or pinacone, but it was identified as the carbinol from the facts that the product gives the same colouration toward concentrated sulphuric acid, before and after fusion, and that the original ketone is reduced to corresponding methane by the same reducing agents but at the boiling temperature of the reacting mixture (See below).

Anal.: Subst. = 0.0649; CO_2 = 0.2107; H_2O = 0.0339 gr.
Found: C = 88.5; H = 5.86%.
Calc. for $C_{23}H_{18}O$ (α-naphthyl-diphenylyl carbinol): C = 89.0; H = 5.81%.

The yield was practically quantitative.

α-Naphthyl-Diphenylyl-Methane, $(\alpha\text{-}C_{10}H_7)(C_6H_5.C_6H_4)CH_2$. α-Naphthyl-diphenylyl ketone was usually reduced in gently boiling glacial

(15) Alcoholic solution of the raw product was decolourized by zinc dust and concentrated hydrochloric acid. The solution was filtered and allowed to crystallise.

acetic acid solution with zinc dust. On pouring the reaction product into water, yellowish crystalline cakes separated and the solution turned milky. The precipitates were recrystallised twice from glacial acetic acid and finally from ligroin with an addition of animal charcoal. It crystallises in thick prisms, melting at 146°C. Purified product does not dissolve in concentrated sulphuric acid, while raw product gives greenish blue colouration toward it. This colouration is due to the presence of a small quantity of the carbinol, which is removed only by recrystallising from glacial acetic acid. The product was proved to be the corresponding methane, α-naphthyl-diphenylyl methane, from its composition and molecular weight. The yield of the pure product did not exceed 40% of the theory.

Anal.: Subst. = 0.0635; CO_2 = 0.2177; H_2O = 0.0365 gr.
Found: C = 93.5; H = 6.41%.
Calc. for $C_{23}H_{18}$ (α-naphthyl-diphenylyl-methane): C = 93.9; H = 6.10%.
Mole. weight: Subst. = 0.270; Camphor = 2.834 mgr.
Depres. of m.p. = 13.0°C.
Found: Mole. weight = 294. Calc. for $C_{23}H_{18}$: Mole. weight = 294.

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STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. IX. CONCLUSION (THE PINACOLINE REARRANGEMENT AS A METHOD OF ESTABLISHING RELATIVE ELECTRONEGATIVITIES OF ORGANIC RADICALS).

By Masao MIGITA.

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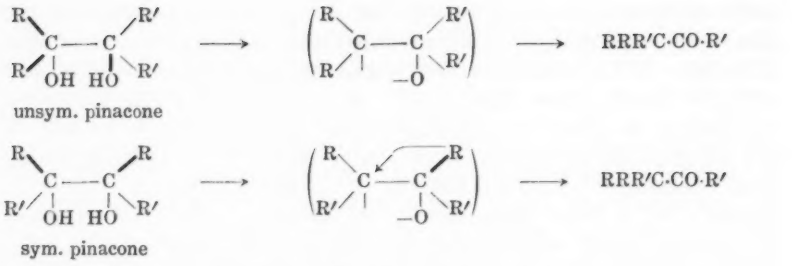
Migration Aptitudes of Organic Radicals. It was Meerwein[1] who explained the mechanism of pinacoline rearrangement by the theory of affinity requirement. His interpretation was originally intended to answer the question which hydroxyl group in *unsymmetrical* pinacone molecule is taken off, and it is impossible to explain why the radical with the larger affinity requirement has greater migration tendency in the rearrangement of a *symmetrical* pinacone.

(1) Meerwein, *Ann.*, **419** (1919), 121.



where thick bars denote larger affinity requirement.

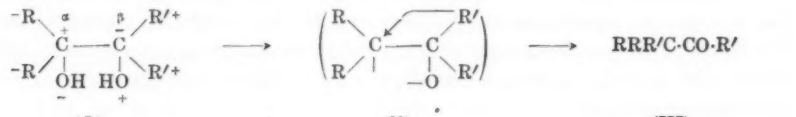
Therefore, Tiffeneau and Lévy[2] were obliged to conclude that a certain migratory aptitude is concerned to each radical, but this property is not necessarily concomitant with its saturation capacity. It must be specially mentioned here that they believed that each radical has its own migration tendency, since this idea has been and is still cherished by many organic chemists. Quite recently Bachmann[3] has stated in his studies on rearrangement of unsymmetrical aromatic pinacones as follows: "The series representing the relative migration aptitudes of the groups in symmetrical pinacones does not hold for the unsymmetrical pinacones. The series for the latter type of molecule may be expressed as follows: $C_6H_5 > CH_3C_6H_4 > CH_3OC_6H_4$. It is especially striking that the *p*-anisyl group, which in the symmetrical pinacone migrates nearly exclusively with respect to the phenyl group, migrates to a lesser extent than the phenyl group when the two groups are in the unsymmetrical molecule."

The reason why Bachmann considered the above result "especially striking" consists in the fact that he understands the migration aptitude as a definite property concerned to each radical.

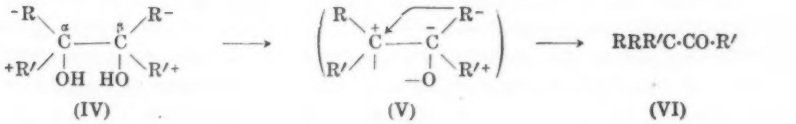
The present author[4] has interpreted the pinacoline rearrangement from the electronic conception of valency any concluded that the order representing the migratory tendency of organic radicals is never constant but it may be reversed depending on the type of molecule subjected to rearrangement. By the author's theory it is quite possible to predict with certainty, the selective migration of radicals by pinacoline rearrangements irrespective of the type of pinacones. It is applicable not only to the rearrangements of pinacones, but also to those of tertiary

(2) Tiffeneau and Lévy, *Compt. rend.*, **176** (1923), 312.
(3) Bachmann, *J. Am. Chem. Soc.*, **54** (1932), 2112–18.
(4) Migita, this Bulletin, **3** (1928), 315–6.

aminoalcohols[5] and of trisubstituted α-glycols[6]. For example, the rearrangements of *unsymmetrical* and *symmetrical* pinacones will be reviewed here, which are expressed schematically as follows:



(I) (II) (III)



(IV) (V) (VI)

where R is more negative than R′.

Strictly speaking, it is not selective migration of radicals, but selective elimination of two hydroxyl groups that comes into question in the rearrangement of *unsymmetrical* pinacones of the type $R_2C(OH).CR'_2(OH)$. As for the selective elimination of these hydroxyl groups, the author has logically deduced that the more negatively polarized hydroxyl group, that is the one bound to carbon atom combined with the more negative groups, should be more ready to be eliminated[7]. Thus, in formula I, the hydroxyl group attached to α-carbon atom will be more readily eliminated, which will result in formation of the fraction of molecule II. It is clear that the migration of a radical from β- to α-carbon atom in the fraction of molecule II can not be said selective, since the both radicals attached to β-carbon atom are the same. It appears, however, as if the more positive radical R′ migrates with respect to the more negative radical R, when the constitution of the pinacoline formed is simply compared with that of the original pinacone.

In the rearrangement of *symmetrical* pinacones the fraction of molecule shown in formula V will be produced intermediately, in which the α-carbon atom has extremely positive polarity, since it has been deprived of a part of its bond-forming electrons with the elimination of the hydroxyl group. Therefore, if one of the two groups attached to β-carbon atom migrates to α-carbon atom in order to make least the

(5) Migita, this Bulletin, **3** (1928), 313–314.
(6) Migita, ibid., **4** (1929), 57–65.
(7) Migita, ibid., **3** (1928), 312–313.

disturbance of the affinity, the group that wanders should be the one that is more negative. Thus migration of the more negative group will chiefly take place in the rearrangement of symmetrical pinacones.

It is concluded that the electronegativities of the substituents in the molecules exert directing influence on the selective elimination of the two hydroxyl groups in the rearrangement of unsymmetrical pinacones and on the selective migration of radicals in the case of symmetrical pinacones.

Relative Electronegativities of Organic Radicals. If migration of radicals in the rearrangement of a pinacone can be predicted by their electronegativities, as shown above, conversely the relative electronegativities of any two radicals R and R′ can be determined from the rearrangement products of the symmetrical or unsymmetrical pinacone containing the two radicals in question. For this purpose, it is sufficient to analyse organic acids produced by the hydrolysis of the rearrangement products. Thus a pinacoline rearrangement offers a simple method to compare electronegativities of organic radicals.

An interesting method to determine relative electronegativities of organic radicals has been given by Kharasch and Marker[8], in which mercury is coupled with two organic radicals R and R′ and the resulting compound is treated with hydrogen chloride. The reaction runs as follows:

$$RHgR' + HCl \rightarrow RH + R'HgCl.$$

It is plausible to assume that the more electronegative of the two radicals R and R′ combines with H^+ to form corresponding hydrocarbon.

Though this method exceeds the pinacoline method in its theoretical interest, it has some disadvantages for practical purpose. Firstly it is generally not so easy to prepare an organomercuric compound containing two given radicals as to prepare a pinacone with the same radicals, and secondly isolation and identification of a mixture of organomercuric chlorides will be in most cases more troublesome work than in the case of a mixture of organic acids[9].

In the pinacoline method the pinacones of either symmetrical or unsymmetrical type which contain the two radicals to be compared may

(8) Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130.

(9) Analysis of a mixture of organomercuric chlorides by its mercury content and that of organic acids by the silver value are applicable only when no high degree of accuracy is demanded.

be used[10], but the symmetrical pinacone is preferable to the other on account of its easiness of preparation. It is especially so when the electronegativities of aromatic radicals are compared, since in this case a simple method is available as described below. Under certain conditions, we may obtain pinacolines, instead of pinacones, when certain aromatic ketones are reduced by glacial acetic acid and zinc dust. It has been proved experimentally as well as theoretically that this direct pinacoline formation from a ketone takes place when both radicals attached to carbonyl group are of high electronegativities[11]. Therefore, if the ketone RCO.R′ is reduced to pinacoline, while the ketone RCO.R″ to pinacone, we can conclude that R′ is more negative than R″. Thus, we can compare the relative electronegativities of aromatic radicals simply from the reduction products of two suitable ketones.

In the foregoing works the author has attempted to compare electronegativities of several highly negative aromatic radicals by pinacoline method and obtained the following series,

$$C_2H_5OC_6H_4 > CH_3OC_6H_4 > \alpha\text{-}C_{10}H_7 > \beta\text{-}C_{10}H_7\,,\ C_6H_5C_6H_4\,,$$

which contains some supplements as well as confirmations to the series of electronegativities given by Kharasch and colaborators. Hithertofore, *p*-anisyl has been considered to be the most electronegative radical but it is found that *p*-ethoxyphenyl radical is by far more negative. β-Naphthyl radical is proved to be more positive than α-naphthyl radical and to rank nearly with diphenylyl radical with respect to its negativity.

Dissociation of Pinacones. The criterion of the stability of a carbon-to-carbon bond is the affinity of the bound radicals for the binding electrons. When the electrons are closely held by both carbon nuclei, the bond is stable; when they are displaced away from one or both nuclei the bond is unstable. Therefore, we can distinguish two cases in unstable linkages between two carbon atoms, thus:

1. Linkage between two radicals of very slight electronegativities, in this case the binding electrons are displaced away from both carbon nuclei.

2. Linkage between an extremely electronegative organic radical and a weakly electronegative one, in which the bond-forming electrons are held at a distance from one nucleus.

(10) It must be remembered that the relation between migration aptitude and electronegativity is reversed in these two cases.

(11) Migita, this Bulletin, **7** (1932), 335, 342, 380.

Dissociation of hexa-aryl ethanes into free radicals and high reactivity of chlorine atom in triarylmethyl chlorides may be cited in illustration of the cases 1 and 2 respectively.

Aromatic pinacones bear close resemblance to hexa-aryl ethanes with respect to the negativities of substituents, and their molecules have unstable linkage of the first kind between the two carbon atoms in chain. Therefore they are naturally assumed to dissociate with production of free radicals under certain conditions, as in the case of hexa-aryl ethanes. This assumption has been confirmed experimentally[12] by the fact that iodomagnesium ketyl radicals with tervalent carbon atoms, RR'Ç.OMgI, are formed when aromatic ketones are reduced by binary mixture of magnesium and its iodide in benzene-ether solution. The formation of free ketyl radicals is recognized by the development of intense colourations, sensible toward oxygen, in the process of reduction.

Besides this, aromatic pinacones undergo another kind of dissociation, that is scission into ketones and carbinols, which is also attributable to the presence of unstable linkage in the molecule. According to literature, the dissociation of aromatic pinacones into ketones and carbinols takes place nearly exclusively at their melting points, tetra-*p*-bromobenzophenone[13] is the only pinacone that undergoes rearrangement and this sort of dissociation simultaneously by the action of acetyl chloride. Being interested in this singular instance, the author has carried out close experiment with tetra-*p*-methoxy-benzopinacone under the same conditions, but dissociation into ketone and carbinol could not be observed.

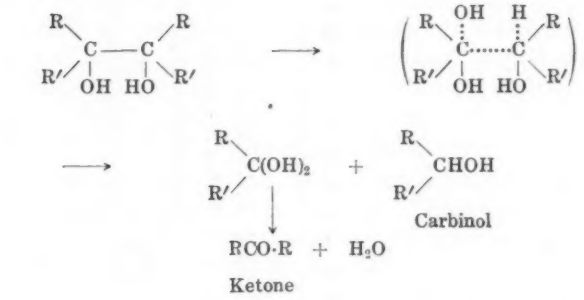
The author has observed that the dissociation into ketone and carbinol takes place not only in aromatic pinacones, but also in *αα*-dimethyl-*β*-acetyl glycol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C(OH)-C(OH)(H)-COCH_3$, an aliphatic glycol containing unstable linkage of the second kind, and that with far greater facility[14].

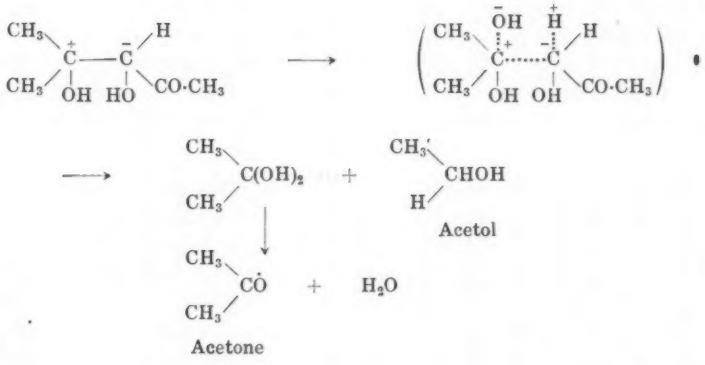
The mechanism of dissociation into ketone and carbinol can be interpreted as follows: In the first stage of the reaction, addition of water takes place at the two adjacent carbon atoms with unstable linkages, which weakens more the bond between these carbon atoms and results in scission of the molecule at this point.

(12) Gomberg and Bailar, Jr., *J. Am. Chem. Soc.*, **51** (1929), 2229.

(13) Montagne, *Rec. trav. chim.*, **43** (1924), 126–142.

(14) Warming with dilute acid or alkali is sufficient to cause the scission of the glycol. Migita, this Bulletin, **4** (1929), 226–7.





Addition of water is naturally expected to occur easier when the polarities of the two carbon atoms are of different signs than when they are same. This is the reason why dimethyl-acetyl glycol with the second kind of unstable linkage exceeds aromatic pinacones with the first kind of unstable linkage in its facility of dissociation into ketone and carbinol.

Reduction of Aromatic Ketones with Highly Negative Groups. Aromatic pinacones are generally obtained by reducing corresponding ketones (i) with zinc dust and glacial acetic acid, (ii) with absolute alcohol under direct sunlight or (iii) with the binary mixture of magnesium and magnesium iodide in benzene-ether solution. The author has reduced several aromatic ketones with highly negative groups by these methods and found that the products are not necessarily pinacones, but they may be pinacolines, carbinols or hydrocarbons under certain conditions (See the Table below).

Reduction of some Aromatic Ketones with Highly Negative Radicals.

Ketone, RCO·R′		Reducing Agents.			
		Glacial acetic acid and zinc dust.		Absolute alcohol under direct sunlight.	Magnesium iodide and magnesium.
R	R′	At room temp.	At higher temp.		
		$R_3C\cdot CO\cdot R$	$R_3C\cdot CO\cdot R$	$R_2C(OH)\cdot C(OH)R_2$	Rosinous matter.
		——	$RR'_2C\cdot CO\cdot R$	$RR'_2C\cdot CO\cdot R$	——
		$RR'C(OH)\cdot C(OH)RR'$	$R_2R'C\cdot CO\cdot R'$	Not reduced.	——
		$RR'C(OH)\cdot C(OH)RR'$	$R_2R'C\cdot CO\cdot R'$	Not reduced.	——
		$RR'CHOH$	$RR'CH_2$	Not reduced.	Pinacone ?
		$RR'CHOH$	$RR'CH_2$	——	——
		$RR'CHOH$	$RR'CH_2$	Not reduced.	$RR'C(OH)\cdot C(OH)RR'$
		——	$R_2C(OH)\cdot C(OH)R_2$ [a]	$R_2C(OH)\cdot C(OH)R_2$ [b]	$R_2C(OH)\cdot C(OH)R_2$ [c]
		$RR'C(OH)\cdot C(OH)RR'$ [d]	$R_2R'C\cdot CO\cdot R'$ [e]	——	$RR'C(OH)\cdot C(OH)RR'$ [d]
		$RR'C(OH)\cdot C(OH)RR'$ [d]	$R_2R'C\cdot CO\cdot R'$ [d]	——	$RR'C(OH)\cdot C(OH)RR'$ [d]
		——	$RR'C(OH)\cdot C(OH)RR'$ [f]	——	——
		——	R_2CH_2 [g]	——	$RR'C(OH)\cdot C(OH)RR'$ [c]

* Unpublished.

a) Zagumenni, *Ber.*, **14** (1881), 1402.
b) Ciamician and Silber, *Ber.*, **33** (1900), 2912.
c) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 249, 254.
d) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.
e) Tiffeneau and Orékhoff, *Bull. Soc. chim.*, **37** (1925), 430.
f) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.
g) Votoček and Krauz, *Ber.*, **42** (1909), 1602.

(i) *Reduction by Zinc Dust and Glacial Acetic Acid.* Aromatic ketones containing highly negative groups are generally reduced by zinc dust and acetic acid to pinacones at ordinary temperature and pinacolines at higher temperature; however, if the negativities of the groups are extremely high, pinacolines are formed even at ordinary temperature as in the case of di-*p*-methoxy-benzophenone.

α-Naphthyl-diphenylyl and β-naphthyl-diphenylyl ketones and αβ-dinaphthyl ketone give carbinols at room temperature and hydrocarbons at higher temperature. This behaviour is considered to concern with sterical problem, rather than with negativity problem.

(ii) *Reduction by Absolute Alcohol under Direct Sunlight.* This method seems inapplicable to ketones which are difficultly soluble in alcohol. It is highly interesting that *p*-methoxy-*p'*-ethoxy-benzophenone is not reduced to pinacone but to pinacoline by this method, while di-*p*-methoxy-benzophenone gives pinacone under the same conditions. We can see, here also, the influence of highly negative substituents on a pinacone in its reactivity.

(iii) *Reduction by Magnesium and Magnesium Iodide.* Reduction by this method has been reported not only to give an excellent yield such as from 75 to 100 percent, with many aromatic ketones, but also to be successful to the ketones to which all other methods fail. The present author has also experienced that β-naphthyl-diphenylyl ketone is reduced to corresponding pinacone only by this method. However, this method seems to give less satisfactory results in the reduction of ketones containing *p*-anisyl radical, for example, Bachmann and Moser[15] observed that 4-methoxy-, 4-methoxy-4'-methoxy-, and 4-methoxy-4'-phenyl-benzophenones were reduced to corresponding pinacones with the yields of 45, 2 and 35% respectively. The author did not succeed in reducing di-*p*-methoxybenzophenone by this method.

In conclusion, the author begs to tender his sincere thanks to Prof. K. Matsubara for his kind advices and encouragements throughout this work.

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Imperial University of Tokyo.

(15) Bachmann and Moser, *J. Am. Chem. Soc.*, **54** (1932), 1126.

g) Votoček and Krauz, *Ber.*, **42** (1909), 1602.